

# Nonlinear Oscillation and Multiscale Dynamics in a Closed Chemical Reaction

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## Oscillatory Chemical Reaction

History.

Systems of Chemical Reaction

Mathematical Modeling

## Main Results

Closed System – The Second Law of Thermodynamics

Far-from-equilibrium Dynamics in  $\mathcal{T}^o$

Near-equilibrium Dynamics in  $\mathcal{T}^n$

Dynamical Transition from  $\mathcal{T}^o$  to  $\mathcal{T}^n$

## Canonical vs Grand Canonical Systems

## Future Work

# History

- ▶ G.T. Fechner, et al. (1828-1900)
- ▶ A. Lotka (1910-1920).
- ▶ V. Volterra (1926)
- ▶ B. Belousov (1951)
- ▶ A.M. Zhabotinsky (1961)
- ▶ Ilya Prigogine and his Brussels school

⋮

BZ reaction—chemical reaction exhibiting oscillatory behavior.

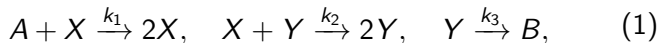
# Systems of Chemical Reaction

- ▶ Open system  
Exchange of both molecules and energy with the surroundings is allowed. (for *in vivo* studies)
- ▶ Closed system  
Exchange of energy but NOT molecules with the surroundings is allowed. (for *in vitro* studies)

Most of currently existing reaction models exhibiting oscillation are open system.

# Irreversible Lotka-Volterra Model

- Irreversible Reaction.



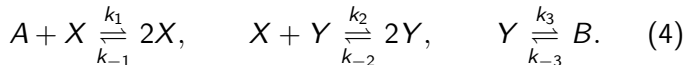
- By the Law of Mass Action, one has

$$\text{Closed system} \quad \begin{cases} \dot{c}_A &= -k_1 c_A x \\ \dot{x} &= k_1 c_A x - k_2 xy \\ \dot{y} &= k_2 xy - k_3 y \\ \dot{c}_B &= k_3 y. \end{cases} \quad (2)$$

$$\text{Open system} \quad \begin{cases} \dot{x} &= k_1 c_A x - k_2 xy \\ \dot{y} &= k_2 xy - k_3 y. \end{cases} \quad (3)$$

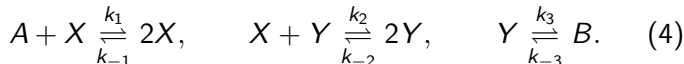
# Reversible Lotka-Volterra System

- Reversible Reaction.



# Reversible Lotka-Volterra System

- Reversible Reaction.



- Rate Equations

$$\left\{ \begin{array}{l} \frac{dx}{dt} = k_1 c_A x - k_{-1} x^2 - k_2 xy + k_{-2} y^2, \\ \frac{dy}{dt} = k_2 xy - k_{-2} y^2 - k_3 y + k_{-3} c_B, \\ \frac{dc_A}{dt} = -k_1 c_A x + k_{-1} x^2, \\ \frac{dc_B}{dt} = k_3 y - k_{-3} c_B. \end{array} \right. \quad (5)$$

# Nondimensionalization

## ► Rescaling

$$\begin{aligned} u &= \frac{k_2}{k_3} x, \quad v = \frac{k_2}{k_3} y, \quad w = \frac{k_1}{k_3} C_A, \quad z = \frac{k_2}{k_3} C_B, \quad \tau = k_3 t, \\ \sigma &= \frac{k_1}{k_2} \ll 1, \quad \frac{k_{-1}}{k_1} = \frac{k_{-2}}{k_2} = \frac{k_{-3}}{k_3} = \varepsilon \ll \sigma. \end{aligned} \quad (6)$$

## ► Dimensionless Form.

$$\left\{ \begin{array}{l} \frac{du}{d\tau} = u(w - v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} = v(u - 1) - \varepsilon v^2 + \varepsilon z \\ \frac{dw}{d\tau} = -\sigma(wu - \varepsilon \sigma u^2). \\ \frac{dz}{d\tau} = v - \varepsilon z. \end{array} \right. \quad (7)$$



# Closed System

- ▶ Linear Conservation Law.

$$u + v + \frac{w}{\sigma} + z = \xi = \text{constant}.$$

- ▶ Reduced system.

$$\begin{cases} \frac{du}{d\tau} &= u(w - v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} &= v(u - 1) - \varepsilon v^2 + \varepsilon \left( \xi - u - v - \frac{w}{\sigma} \right) \\ \frac{dw}{d\tau} &= -\sigma(wu - \varepsilon \sigma u^2). \end{cases} \quad (8)$$

# Closed System

Denote

$$\mathcal{T} = \left\{ (u, v, w) \in \mathbb{R}^3, u, v, w > 0, \text{ and } u + v + \frac{w}{\sigma} \leq \xi \right\}.$$

Then  $\mathcal{T}$  is positively invariant under the flow induced by the closed system (8), and  $\mathcal{T}$  is called the reaction zone.

System (8) has a unique interior equilibrium point  $P \in \mathcal{T}$  at which its Jacobian matrix has three real eigenvalues

$$|\lambda_1 + (1 + \varepsilon)| \sim \varepsilon^2, \quad |\lambda_2 + \varepsilon\xi| \sim \varepsilon^2, \quad |\lambda_3 + \sigma\varepsilon^2\xi| \sim \sigma^2\varepsilon^3.$$

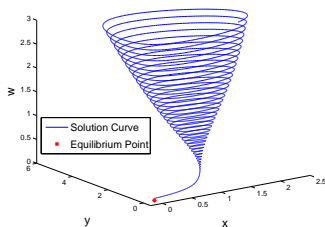
Thus  $P$  is an asymptotically stable node.

# The Second Law of Thermodynamics

$P$  is the global attractor of system (8) in  $\mathcal{T}$ . The free energy

$$L = u \ln \left( \frac{u}{u^*} \right) + v \ln \left( \frac{v}{v^*} \right) + \frac{w}{\sigma} \ln \left( \frac{w}{w^*} \right) + \left( \xi - u - v - \frac{w}{\sigma} \right) \ln \left( \frac{\xi - u - v - \frac{w}{\sigma}}{\xi - u^* - v^* - \frac{w^*}{\sigma}} \right)$$

serves as the Lyapunov function, where  $P = (u^*, v^*, w^*)$ .



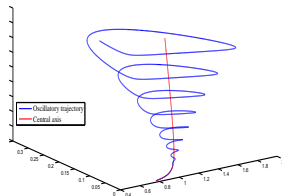
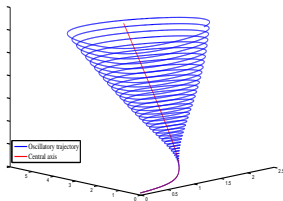
## Far-from-equilibrium – Oscillation Zone

There exist  $\mathcal{T}^0 \subset \mathcal{T}$  and a 1D curve  $W_{\sigma,\varepsilon}^0 \subset \mathcal{T}^0$  such that all the oscillatory solutions in  $\mathcal{T}^0$  go around  $W_{\sigma,\varepsilon}^0$ . The total oscillation time is  $T_o \sim -\frac{\ln \sigma}{\sigma}$ . For fixed  $w_0 > w_1$ , there are at least  $N$  complete oscillations by  $2\pi$  with  $w$  decreasing from  $w_0$  to  $w_1$ , where  $N \geq \frac{\ln w_0 - \ln w_1}{2\pi K} - 1$ . And  $W_{\sigma,\varepsilon}^0$  is approximately given by

$$W_{\sigma,\varepsilon}^0 \sim \left\{ (u, v, w), \quad u = \frac{1}{1+\sigma}, \quad v = w, \quad w \in [\underline{w}, \bar{w}] \right\}.$$

Large  $\xi$

Small  $\xi$



## Existence of $W_{\sigma,\varepsilon}^o$

Consider the partially perturbed system where  $\varepsilon = 0$

$$\begin{cases} \dot{u} = u(w - v) \\ \dot{v} = v(u - 1) \\ \dot{w} = 0 \end{cases} \Rightarrow \begin{cases} \dot{u} = u(w - v) \\ \dot{v} = v(u - 1) \\ \dot{w} = -\sigma w u \end{cases} \quad (9)$$

which admits a stable invariant manifold

$$W_{\sigma}^o = \left\{ (u, v, w), \quad u = \mu_{\sigma} = \frac{1}{1 + \sigma}, \quad v = w \geq 0 \right\}.$$

with Lyapunov function

$$E_{\sigma} = (1 + \sigma) \left[ u - \mu_{\sigma} - \ln \left( \frac{u}{\mu_{\sigma}} \right) \right] + \left[ v - w - w \ln \left( \frac{v}{w} \right) \right]$$

# Normal Hyperbolicity of $W_\sigma^0$ ?

## ► Generalized Lyapunov Type Numbers

$$\begin{aligned}\gamma_L(W_\sigma^o) &= \overline{\lim}_{t \rightarrow -\infty} \left\| \pi_p^N D\phi_t(W_\sigma^o) \right\|^{\frac{1}{t}} < 1, \\ \sigma_L(W_\sigma^o) &= \overline{\lim}_{t \rightarrow -\infty} \frac{\log \left\| D\phi_t(W_\sigma^o) \pi_p^T \right\|}{\log \left\| \pi_p^N D\phi_t(W_\sigma^o) \right\|} \geq 2,\end{aligned}$$

## ► Exponential Dichotomy

$$\begin{aligned}u &\rightarrow \mu_\sigma + x, \quad v \rightarrow v + w, \quad w \rightarrow w, \quad X = (x, y)^T \\ \begin{cases} \sigma X' = A_\sigma(w)X + G_{\sigma,\varepsilon}(X, w) \\ w' = F_{\sigma,\varepsilon}(X, w), \end{cases} & A_\sigma(w) = \begin{bmatrix} 0 & -\mu_\sigma \\ \frac{w}{\mu_\sigma} & -\sigma\mu_\sigma \end{bmatrix} \end{aligned} \quad (10)$$

where  $Re(\lambda(A_\sigma)) \leq -\frac{\sigma\mu_\sigma}{2}$  as  $w \geq \frac{\sigma^2\mu_\sigma^2}{4}$ .

# Proof–Sakamoto (1990)

## ► Modified system

$$\begin{cases} \sigma X' = A_\sigma(w)X + G_{\sigma,\varepsilon}(X, w) \\ w' = F_{\sigma,\varepsilon}(X, w)\chi_{[\sigma^2, \sigma\xi]}(w) \end{cases} \quad (11)$$

$$\begin{cases} X(t) = \frac{1}{\sigma} \int_{-\infty}^t \Phi_\sigma(t, s, w(s)) G_{\sigma,\varepsilon}(X, w) ds \\ w(t) = H(\eta, X)(t) < \infty, \quad w(0) = \eta \in [\sigma^2, \sigma\xi]. \end{cases}$$

$$\mathcal{F}(X) = \frac{1}{\sigma} \int_{-\infty}^t \Phi_\sigma(t, s, H(\eta, X)(s)) G_{\sigma,\varepsilon}(X, H(\eta, X)(s)) ds.$$

►  $\mathcal{F}$  is a contraction as  $|X| \leq \delta$  for some  $\delta \Rightarrow \mathcal{F}(X_\eta^*) = X_\eta^*$ .

►  $W_{\sigma,\varepsilon}^o = \{(u = \mu_\sigma + x_w^*(0), v = w + y_w^*(0), w), w \in [\sigma^2, \sigma\xi]\}$ .

## Closer Look of Oscillatory Behavior

Define

$$\mathcal{T}_1^o = \{(u, v, w) \in \mathcal{T} : w \geq \sigma\}, \quad \mathcal{T}_2^o = \{(u, v, w) \in \mathcal{T} : w \geq \sigma^2\},$$

$$\Omega_- = \{(u, v, w) \in \mathcal{T} : v < w\}, \quad \Omega_+ = \{(u, v, w) \in \mathcal{T} : v > w\}.$$

For  $\varepsilon \ll \sigma \ll 1$  and some  $1 < \alpha < 2$ ,

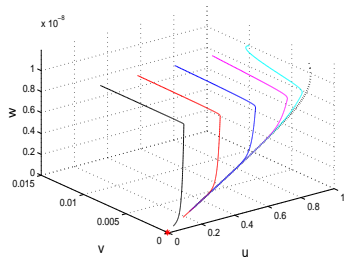
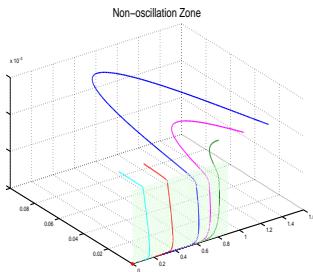
- ▶  $\mathcal{T}_1^o \subset \mathcal{T}^o \subset \mathcal{T}_2^o$ .
- ▶ In  $\Omega_+$ ,  $\frac{w_{2k+1}}{w_{2k}} \sim 1$  and  $\frac{E_{2k+1}}{E_{2k}} \sim 1$ .
- ▶ In  $\Omega_-$ ,  $\frac{w_{2k+2}}{w_{2k+1}} < e^{-\sigma c_1(w_0, E_0)}$  and  $\frac{E_{2k+2}}{E_{2k+1}} < e^{-\sigma c_2(w_0, E_0)}$ .
- ▶ At the bottom of  $\mathcal{T}^o$  where  $w \sim \sigma^\alpha$ ,  $E \sim (\alpha - 2)\sigma^\alpha \ln \sigma$ .



## Near-equilibrium – Non-oscillation Zone

There exist  $\mathcal{T}^n \subset \mathcal{T}$  and a 2D strongly stable invariant manifold  $M_{\sigma,\varepsilon}^n \subset \mathcal{T}^n$  and a 1D stable curve  $W_{\sigma,\varepsilon}^n \subset M_{\sigma,\varepsilon}^n$ . The “total time” in  $\mathcal{T}^n$  is  $T_n \sim -\frac{\ln \varepsilon}{\varepsilon}$ . And

$$W_{\sigma,\varepsilon}^n \sim \left\{ (u, v, w), \quad v = \varepsilon \frac{\xi - u}{1 - u}, \quad w = \sigma \varepsilon u, \quad u \in [0, \bar{u}], \bar{u} < 1 \right\}.$$



## Existence of $M_{\sigma,\varepsilon}^n$

Under the following transformation

$$u \rightarrow u, \quad v \rightarrow \varepsilon v, \quad w \rightarrow \sigma \varepsilon w.$$

system (8) becomes

$$\begin{cases} \frac{du}{d\tau} &= \varepsilon [u(\sigma w - v) - (\sigma u^2 - \varepsilon^2 v^2)] \\ \frac{dv}{d\tau} &= v(u - 1) - \varepsilon^2 v^2 + (\xi - u - \varepsilon v - \varepsilon w) \\ \frac{dw}{d\tau} &= -\sigma u(w - u). \end{cases} \quad (12)$$

By Fenichel's Theorem, critical manifold

$$M_0^n = \left\{ (u, v, w), \quad v = \frac{\xi - u}{1 - u}, \quad u, w \in [0, \bar{u}], \bar{u} < 1 \right\}$$

is normally hyperbolic and thus persists under the perturbation.

# Existence of $W_{\sigma,\varepsilon}^n$

## ► Reduced System

$$\begin{cases} \frac{du}{d\tau_1} = \frac{\varepsilon}{\sigma} [u(\sigma w - h_{\sigma,\varepsilon}(u, w)) - (\sigma u^2 - \varepsilon^2 h_{\sigma,\varepsilon}^2(u, w))] \\ \frac{dw}{d\tau_1} = -u(w - u). \end{cases} \quad (13)$$

Critical manifold

$$W_0^n = \{(u, w), \quad w = u \in [\underline{u}, \bar{u}], 0 < \underline{u} < \bar{u} < 1\}$$

is normally hyperbolic and thus persists under the perturbation.

# In the Vicinity of Equilibrium $P$

- ▶ Stable Invariant manifold may be applied.
- ▶ Further Rescaling

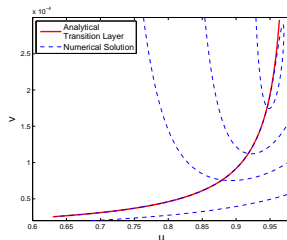
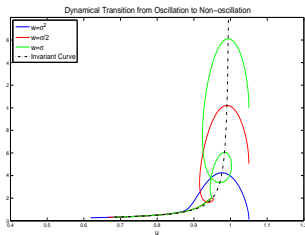
$$u \rightarrow \sigma \varepsilon u, \quad v \rightarrow v, \quad w \rightarrow w, \quad \tau_2 = \frac{\varepsilon}{\sigma} \tau_1.$$

yields

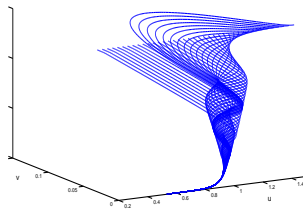
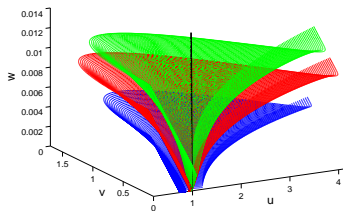
$$\begin{cases} \frac{du}{d\tau_2} = u(\sigma w - h_{\sigma,\varepsilon}) - (\sigma^2 \varepsilon u^2 - \frac{\varepsilon}{\sigma} h_{\sigma,\varepsilon}) \\ \frac{dw}{d\tau_2} = -\sigma^2 u(w - \sigma \varepsilon u). \end{cases} \quad (14)$$

# Dynamical Transition from $\mathcal{T}^o$ to $\mathcal{T}^n$

The passage of entering the non-oscillation zone  $\mathcal{T}^n$  from the oscillation zone  $\mathcal{T}^o$  is around the portion of the central axis connecting  $W_{\sigma,\varepsilon}^o$  and  $W_{\sigma,\varepsilon}^n$ . This is exactly where the transition occurs.



# Dynamical Transition from $\mathcal{T}^o$ to $\mathcal{T}^n$



# A General Network of Chemical Reactions

Consider a system of chemical reactions whose rate equations, by the law of mass action, are given by

$$X' = V(X) = AR(X) \quad (15)$$

where  $A = (a_{ij})$  is the stoichiometric matrix and  $R_i(X) = r_i^f(X) - r_i^b(X)$  with

$$r_i^f(X) = k_i \prod_{a_{ji} < 0} x_j^{-a_{ji}}, \quad r_i^b(X) = k_{-i} \prod_{a_{ji} > 0} x_j^{a_{ji}}.$$

Rewrite equation (15) as

$$\begin{cases} X_1' = F_1(X_1, X_2) \\ X_2' = F_2(X_1, X_2). \end{cases} \quad (16)$$

## Canonical System and Grand Canonical System

- ▶ Canonical System.

By the linear conservation law  $M_1 X_1 + M_2 X_2 = \xi$ , equation (16) is reduced into

$$X_1' = F_1(X_1, M_2^{-1}(\xi - M_1 X_1)). \quad (17)$$

- ▶ Grand Canonical System.

By treating  $X_2 = X_2^0$  as a constant vector, equation (16) is reduced into

$$X_1' = F_1(X_1; X_2^0). \quad (18)$$



# Canonical System and Grand Canonical System

- ▶ (Gibb's Principle) For given  $X_2^0$  and  $\xi$ , let  $X_c^*$  and  $X_{gc}^*$  be the equilibrium points of systems (17) and (18), respectively. If  $X_2^0 = M_2^{-1}(\xi - M_1 X_c^*)$ , then  $X_c^* = X_{gc}^*$ .
- ▶ Systems (17) and (18) share the “same” Lyapunov functions.
- ▶ Both  $X_c^*$  and  $X_{gc}^*$  are all asymptotically stable nodes.

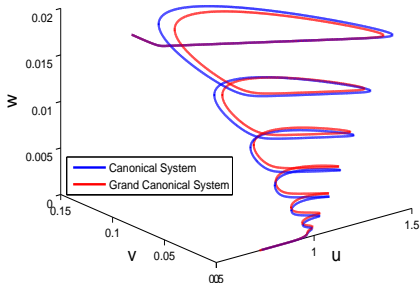
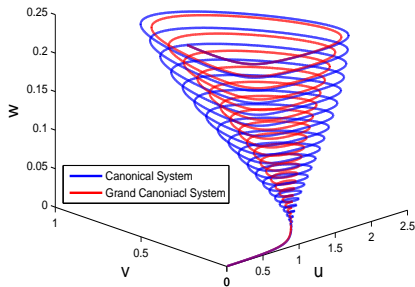
$$\text{Recall} \quad \left\{ \begin{array}{l} \frac{du}{d\tau} = u(w - v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} = v(u - 1) - \varepsilon v^2 + \varepsilon z \\ \frac{dw}{d\tau} = -\sigma(wu - \varepsilon \sigma u^2) \\ \frac{dz}{d\tau} = v - \varepsilon z. \end{array} \right. \quad (19)$$

$$\text{Canonical} \quad \left\{ \begin{array}{l} \frac{du}{d\tau} = u(w - v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} = v(u - 1) - \varepsilon v^2 + \varepsilon \left( \xi - u - v - \frac{w}{\sigma} \right) \\ \frac{dw}{d\tau} = -\sigma(wu - \varepsilon \sigma u^2) \end{array} \right. \quad (20)$$

$$\text{Grand Canonical} \quad \left\{ \begin{array}{l} \frac{du}{d\tau} = u(w - v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} = v(u - 1) - \varepsilon v^2 + \varepsilon z \\ \frac{dw}{d\tau} = -\sigma(wu - \varepsilon \sigma u^2) \end{array} \right. \quad (21)$$

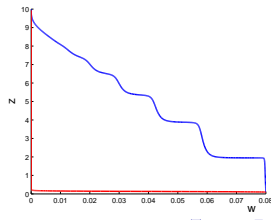
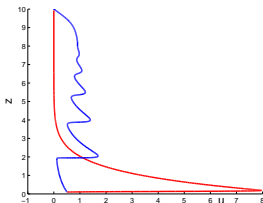
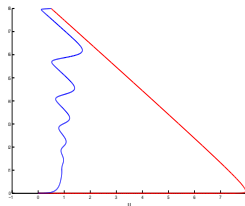
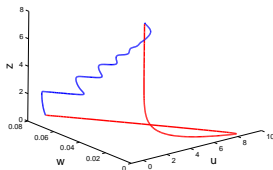
# Canonical System vs Grand Canonical System

- System (20) admits similar dynamics as (21) does.



# Canonical System vs Grand Canonical System

- When  $\nu = \nu^* \sim \varepsilon$ .



# Future Work

- ▶ Effect of noise on the dynamics
  - ▶ Macroscopic level– Fokker-Planck equation
  - ▶ Microscopic level– chemical master equation(in progress)
- ▶ Dissipative perturbation of conserved system.

Thank you!